Elemental Analysis of Glass by Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS)

1 Scope

1.1 Introduction

This document provides the procedure for the identification and quantitation of numerous elements in glass by Geologist/Forensic Examiners in the Trace Evidence Unit (TEU). The concentrations of selected elements in glass serve to chemically characterize the source of the glass. The concentrations of several elements are intentionally controlled by the manufacturers to impart specific end-use properties to a particular glass product. These manufacturer-controlled elements help to chemically characterize a glass fragment by placing it into a particular product use class. The concentrations of trace elements are generally not controlled by the manufacturers. Subtle and distinct differences in the concentrations of manufacturer-controlled elements and uncontrolled trace elements provide a means of differentiating among glasses made by different manufacturers, among glasses from different product lines of a single manufacturer, and over time along an individual production line of glass from a single manufacturer.

This standard operating procedure (SOP) is implementing through incorporation by reference the ASTM International E2927, Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using LA-ICP-MS for Forensic Comparisons. ASTM E2927 is on the Organization of Standard Area Committees (OSAC) Registry of Approved Standards.

1.2 Principle

This procedure is for the quantitative analysis of seventeen elements: lithium (Li), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), iron (Fe), titanium (Ti), manganese (Mn), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba), lanthanum (La), cerium (Ce), neodymium (Nd), hafnium (Hf), and lead (Pb) by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the forensic analysis of glass fragments. The precision, accuracy, and limits of detection of these elements were established during the validation of the method. Silicon (Si) is also monitored for use as a normalization standard. Additional elements may be added as needed, for example, tin (Sn) can be used to monitor the orientation of float glass fragments. The concentrations of the elements listed above range from the low parts per million ($\mu g g^{-1}$) to percent (%) levels in soda-lime-silicate glass, the most common type encountered in forensic cases. This standard method may be applied for the quantitative analysis of other glass types; however, some modifications in the standard reference glasses and the element menu may be required.

1.3 Specimens

This procedure is used for the analysis of small fragments of broken glass objects such as: windows, windshields, or containers. The method consumes approximately 0.4 to 2 µg of glass per replicate and is suitable for the analysis of full thickness samples as well as irregularly shaped fragments as small as 0.1 mm by 0.4 mm in dimension.

2 Equipment/Materials/Reagents

- Cleaning solution (e.g., Cavicide, Windex)
- Compressed air
- Deionized water (18.2 megohm-cm or higher)
- Distilled water
- Ethanol (American Chemical Society (ACS)
- Glass Standard Reference Materials (SRMs) NIST 612, Schott FGS2, Deutsche Glastechnische Gesellschaft DGG1 or equivalent
- Grinder/Polisher
- Helium
- Kimwipes, Techwipes, or equivalent low lint paper tissue
- Laboratory coat
- Nitrile gloves or equivalent
- NWR UP213 Nd:YAG Laser Ablation System or equivalent with an accompanying personal computer containing the instrument software (i.e., Meolaser for the NWR UP213)
- Safety goggles
- Sonicator
- Tape, double sided
- Thermo Scientific iCAP RQ ICP-MS or equivalent with an accompanying personal computer containing the instrument software (i.e., Qtegra for the iCAP RQ)
- Thermo Scientific Solution 5A
- Tweezers

3 Standards and Controls

3.1 *Calibration:* A single point calibration curve using a single glass standard is used for quantitation. Calibration standards must be matrix-matched to the sample and well characterized. For routine soda-lime-silicate glass analysis, use FGS2. For other glass types, NIST 612 may be used.

3.1.1 Analyze at least three spots of the calibration standard at the beginning of the analytical sequence, and at least three spots of the calibration standard the end of the analytical sequence.

3.2 *Accuracy and Precision:* In addition to the calibration standard, measure at least six spots of an additional glass standard reference material, such as DGG1, with each sample set/analytical sequence as a check of accuracy and precision.

3.2.1 Assess each standard glass measured against the control charts for the method. Mean concentration values have been established or verified for each of the glass SRMs by measuring at least six spots over five days. From these analyses, a standard deviation was calculated. See Table 1 for concentrations and standard deviations. A control is acceptable if the calculated mean value of each element is within three standard deviations (± 3SD) of the control chart mean, and the relative standard deviation (RSD) is ≤10%.

Table 1: Control Chart Values

	Mean Measured Concentration, ppm ($\mu g g^{-1}$)			**Standard Deviation, ppm ($\mu g g^{-1}$)**		
Element	SRM 612	FGS 2	DGG1	SRM 612	FGS 2	DGG1
Li	47.322	29.237	27.226	1.302	0.703	0.722
Mg	89.478	23,459.200	26,159.780	5.505	358.690	1,203.177
Al	10,789.65	7,433.527	6,858.389	143.672	140.510	364.629
K	75.723	4,624.191	3,061.981	5.971	58.391	80.143
Ca	80,451.320	60,229.810	52,904.730	1,007.938	658.563	4,246.259
Ti	40.131	330.123	816.230	0.912	4.932	29.250
Mn	39.701	223.335	66.354	0.404	2.893	2.398
Fe	74.623	2,625.711	1,251.422	7.004	30.698	35.280
Rb	30.362	35.763	2.214	0.366	0.534	0.054
Sr	79.160	262.978	16.365	1.112	3.092	0.676
Zr	37.968	232.485	27.095	0.689	4.244	0.998
Ba	40.478	209.655	66.620	0.845	2.900	2.778
La	36.001	18.957	2.047	0.650	0.329	0.083
Ce	39.085	24.098	3.979	0.565	0.361	0.151
Nd	36.357	26.071	2.038	0.555	0.407	0.073
Hf	38.811	15.558	0.079	0.603	0.269	0.037
Pb	42.469	24.798	6.147	0.717	0.543	0.194

3.2.2 When precision (measured as RSD) among the glass replicate measurements for SRMs is >10% for elements present at readily measurable levels, take appropriate measures to determine the cause of the discrepancy. When the measured concentrations of several elements in a standard glass have relative standard deviations >10%, measurement of additional standard glass samples may be necessary. When the measured concentrations of several elements in the additional standard glass have relative standard deviations >20%, the run will be discontinued.

3.3 *Normalization:* The use of a normalization standard is needed to adjust for differences in ablation yield between the ablated materials (i.e., to normalize the signal). Because silicon is present as a major component in all soda-lime-silicate glass (~70 to 72 % as SiO_2), use ^{29}Si as the normalization standard during the analysis of these glass samples. If analyzing other

glass types, the concentration of the normalization standard used must be determined prior to quantitative analysis. In the Qtegra software, select "IS" for the element selected as the normalization standard.

3.4 Store glass SRMs, such as DGG1, FGS2, and NIST 612 at ambient temperature and pressure in separate, closed containers to prevent deleterious change. Glass standards maintained in this fashion have an indefinite shelf life.

3.4.1 When the glass SRM samples have been ablated multiple times and there is no longer enough of a flat surface for analysis, they can be re-polished or replaced.

4 Sampling

4.1 If possible, select several samples from each exemplar item to represent the range of potential compositions of the glass. When sufficient glass is available, choose at least three replicate specimens per source.

4.2 For the known source, take a minimum of nine measurements (from at least three fragments if possible) and calculate the mean for each element.

4.3 For each questioned fragment, take as many replicates (spots) as possible, with a minimum of three, and calculate the mean for each element.

5 Procedures

5.1 *Startup*

5.1.1 Turn the main power on the ICP-MS on. Wait at least 30 minutes.

5.1.2 Turn on the ICP-MS chiller and set to 20°C. Wait at least one hour.

5.1.2.1 Ensure that the water level is at least ¾ full. If needed, add distilled water.

5.1.2.2 Determine whether the water is clean by examining the water and the filter. If the water appears to have a distinct color or there is visible particulate in the filter, clean or change the filter. If the water is dirty, drain the chiller per manufacturer's instructions and refill with clean, distilled water.

5.1.2.2.1 Clean the filter by removing it from the chiller and placing it in an ultrasonic bath (sonicator) for several minutes in clean water. If necessary, add dilute bleach to the bath. Repeat until filter is clean. When clean, rinse filter in clean water, and reinstall.

5.1.2.2.2 If the filter cannot be sufficiently cleaned, replace it with a new filter.

5.1.3 Turn on the chiller attached to the laser ablation system. Check that the water level is at least ¾ full. If needed, add deionized water. If the water is dirty, drain the chiller per the manufacturer's instructions and refill with clean, deionized water.

5.1.4 Turn on the switch in the back of the laser to start the system and open the Meolaser software by selecting the <NWR> icon.

5.1.5 Select <Purge> to purge the ablation cell for at least 120 seconds.

5.1.6 On the ICP-MS computer, open Qtegra and Instrument Controls and select "STDS Laser" mode in Instrument Controls.

5.1.7 After the purge is complete, select <ON> in Instrument Controls to ignite the plasma.

5.1.8 Let the plasma warm up for at least 30 minutes.

5.1.9 Turn on the helium by the switch on the wall. The pressure should be ~10 psi. If not, adjust the wall gauge.

5.1.10 In Meolaser, select <Mass Flow>. Set the flow rate to 800 mL/min. When the flow rate reaches the set point, purge the ablation cell again.

5.1.11 In Meolaser, set the following parameters:
Mode: continuous
Energy: 0%
Rep Rate: 1Hz
Spot Size: ?µm

5.1.12 Fire the laser for 10 minutes with the shutter closed.

5.2 *Tuning*

5.2.1 Prior to analysis, on the day it is used, tune the ICP-MS according to the manufacturer's recommendations and those determined from the instrument validation.

5.2.2 After warming up the laser and the plasma (see section 5.1), use NIST 612 programmed with an eight-minute line to tune the ICP-MS.

5.2.3 Use the following conditions in Meolaser:
Mode: continuous
Energy: 80%
Rep Rate: 10 Hz
Spot Size: 80 µm
Passes: 1
Scan Speed: 10
Depth/Pass: 5

5.2.4 In Instrument Control (ICP-MS), ensure that the instrument is in "STDS Laser" mode and run the "Autotune Wizard" for "Source Tune High Laser."

5.2.5 In Instrument Control (ICP-MS), run the "Performance Report Wizard" for "Source Tune High Laser." If the Performance Report shows failures, re-run the tune and Performance report. Repeated failure of the sensitivity or stability test reports may indicate that the system needs cleaning or maintenance. Follow the guidance in the iCAP RQ instrument manual for cleaning and maintenance. If the instrument continues to fail the performance report after cleaning and maintenance, the instrument will be taken out of service until the failure is remediated.

5.3 *Mass Calibration*

5.3.1 Conduct a mass calibration every two weeks if the instrument is in regular use (i.e., running several times a week). If the instrument is being run intermittently, conduct the mass calibration prior to analysis.

5.3.2 Place the ICP-MS into solution mode.

5.3.3 In Instrument Control (ICP-MS), ensure that the instrument is in "STD" mode and run the "Mass Calibration Wizard," using the Thermo Scientific Solution 5A.

5.3.3.1 If the mass calibration fails, rerun the "Mass Calibration Wizard," selecting "Course Mass Calibration" mode.

5.3.3.2 If running the Course Mass Calibration still fails, run the "Full Detector Tune Wizard." If the instrument fails after at least two attempts, the instrument may need to be cleaned (see section 4.4.5) or serviced by the manufacturer. If the instrument continues to fail after cleaning and maintenance, the instrument will be taken out of service until the failure is remediated.

5.4 *Sample Preparation*

5.4.1 If necessary, clean the samples to remove surface contamination. This can be done by washing or pre-ablation, or both.

5.4.2 Wash samples with an appropriate solvent with or without sonication. Appropriate solvents should be chosen based on their ability to remove the contamination without altering the glass and can include soap and water, organic solvents, or bleach. Following washing, rinse the samples with deionized water, followed by ethanol (or equivalent). Allow to dry completely.

5.4.2.1 See section 5.5.3.2 for pre-ablation settings. Pre-ablation is done immediately prior to signal acquisition as part of the program settings.

5.4.3 Load samples into the ablation cell.

5.4.3.1 Secure samples in the ablation cell using double-sided tape or other appropriate adhesive. If necessary, use a glass microscope slide or equivalent to raise the samples such that they are all at approximately the same height.

5.4.3.2 Purge the ablation cell for at least 120 seconds.

5.5 *Analysis*

5.5.1 Follow instrument startup and warmup per section 5.1.

5.5.2 Tune the instrument per section 5.2.

5.5.3 In Meolaser, open a new experiment and choose spots on each glass sample, the number of which is specified in sections 4.1 and 4.2. Select spots (i.e., replicate measurements) on different locations within the fragment. Place the locations of each spot sufficiently apart from each other to avoid possible debris from other ablation halos. Label each spot with its FBI Laboratory Item Number, followed by a spot identifier (e.g. Item 1a, Item1b …). Ensure that each spot is in focus.

5.5.3.1 Set the following analysis conditions in Meolaser:
Mode: continuous
Passes: 1
Depth: 5 µm
Energy: 20% (Fluence ~10 J/cm^2)
Rep Rate: 10 Hz
Spot Size: 50 µm
Dwell Time: 60 seconds
Select “Close Shutter after Scan” box
Select “Enable Pre-Ablation Pass” box

5.5.3.2 Set the following conditions for the pre-ablation in Meolaser:
Energy: 20%
Rep Rate: 10 Hz
Spot Size: 80 µm
Dwell Time: 20 seconds
Select <Apply Settings to Laser> and <OK>

5.5.3.3 Select <Run> and use the following conditions:
Passes: 1
Pre-ablation: online
Ablation: online
Select "Enable Laser During Scans" box
Laser Warmup: 20 seconds

5.5.4 In "Qtegra" (ICP-MS), open a new LabBook from the "Glass" template with "trQuant" evaluation per the manufacturer's instructions and save it a unique identifier.

5.5.4.1 Input sample information run order using spots set up in Meolaser. Change spot labels and NWR list.

5.5.4.2 Select <Schedule> and <OK>, then <Run>.

5.5.5 Each data acquisition sequence will consist of a 20-30 second gas blank (i.e., background), followed by 50-60 seconds of sample ablation, followed by at least 60 seconds of post-ablation blank (i.e., washout time). Absolute times will vary according to sample requirements (e.g., fragment size, glass type, etc.).

5.6 *Data Processing*

5.6.1 Select "Average Intensity Data" under "Evaluation Results" folder in Qtegra and add two regions.

5.6.2 Select "Regions" under "Method Parameters" folder and rename the regions "Gas Blank" and "Ablation" and define their extent.

5.6.2.1 Choose the as Blank region from the flat portion of the scan collected before the ablation. The Gas Blank should be approximately 20 seconds.

5.6.2.2 Choose the Ablation region from the flattest portion of the scan collected during ablation. The Gas Blank should be approximately 50 seconds when a sufficiently large flat region is present, but may be as little as 30 seconds. Normalize the ablation region to the ^{29}Si internal standard signal.

5.6.3 Export the data.

5.7 *Shutdown*

5.7.1 Purge the ablation chamber for at least 120 seconds.

5.7.2 Turn off the helium carrier gas.

5.7.3 Turn the mass flow to zero when the regulator is approximately zero.

5.7.4 Close the Meolaser software and switch the laser off.

6 Interpretation of the Analytical Results

6.1 Following the recommendations of Trejos et al (2013), use a modified 4σ confidence interval as the comparison criterion for the comparative analysis of glass fragments by LA-ICP-MS. If the average elemental concentration for any element in the item being compared falls outside of the modified 4σ confidence interval for that element in an exemplar sample, the items are considered distinguishable (an exclusion conclusion).

6.2 If measured elemental concentrations are between the limit of detection and the limit of quantitation of the instrument, measured concentration values are unreliable and may produce unacceptably high RSDs. In this case, reanalysis of the samples is not useful. While it is possible to report the presence of an element if the concentration of the element is between the limit of detection and the limit of quantitation, the elements will not be considered during a comparison.

6.3 The detection limits of this method vary slightly from day to day. Approximate method detection limits have been stated in the validation records for the Thermo Scientific iCAP RQ. These values may be used as a guide, but a better approximation can be determined for each particular case when needed.

7 Calculations

A modified 4σ confidence interval is calculated by taking either the measured standard deviation or 3% of the average for each element, whichever is greater, and multiplying it by four. The confidence interval for an element is the average value of the elemental concentration ± the modified 4σ.

8 Measurement Uncertainty

Uncertainty values for each element were determined during instrument validation (see LA-ICP-MS Validation folder). Additional uncertainty information for LA-ICP-MS can be found in the appendix of ASTM E2927.

9 Limitations

9.1 Fragments smaller than 0.4 mm x 0.1 mm may be too small for analysis with the current operating conditions.

9.2 Laser ablation may change the refractive index of the glass fragment. Therefore, refractive index measurements on glass fragments that have been ablated is not recommended.

10 Safety

10.1 Commercial laser ablation units are enclosed type I lasers. However, laser systems typically used for analysis of glass generate high energy radiation that may pose serious risks to eye safety if exposed to the eye. Interlocks must not be bypassed or disconnected.

10.2 ICP-MS instruments generate high amounts of radiofrequency energy in their RF power supply and torch boxes that is potentially hazardous if allowed to escape. Safety devices and safety interlocks must not be bypassed or disconnected.

10.3 Breaking glass can cause glass fragments to be ejected in unpredictable trajectories. Use caution to break the glass in a way that minimizes blowback. Broken glass can cause cuts and damage to eyes and exposed skin. PPE must be worn when handling or breaking glass including: gloves, safety glasses, and a laboratory coat.

11 References

- ASTM International, Standard Test Method for Determination of Trace Elements in Soda-Lime Glass Samples Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Forensic Comparisons (E2927).

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- FBI Laboratory Safety Manual (current version)

- Thermo Scientific iCAP RQ manual.

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Approval

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